2. Stationary perturbation method

Introduction

$$H = H^0 + H' \tag{1}$$

The eigenstates and eigenfunctions of H^0 are known

If E_k^0 is non-degenerated

$$H^0\Psi_k = E_k^0\Psi_k. \tag{2}$$

First-order correction

$$E_k^{(1)} = \langle\Psi_k|H'|\Psi_k\rangle = H'_{kk} \tag{3}$$

Eigenfunctions

$$(H^0 - E_k^0)\Psi_k^{(1)} + (H' - E_k^{(1)})\Psi_k = 0. \tag{4}$$

$$\Psi_k^{(1)} = \sum_{m\neq k} \frac{H'_{mk}}{E_k - E_m}\Psi_m \tag{5}$$

Second-order correction to the energy

$$E_k^{(2)} = \langle\Psi_k|H' - E_k^{(1)}|\Psi_k^{(1)}\rangle. \tag{6}$$

$$E_k^{(2)} = \sum_{m\neq k} \frac{|H'_{km}|^2}{E_k - E_m} \tag{7}$$

If E_k^0 is degenerated

$$H^0\Psi_{kr} = E_k^0\Psi_{kr}; \qquad r = \overline{1,g}, \tag{8}$$

ahol g – degree of degeneration

$$\langle\Psi_{kr}|\Psi_{ks}\rangle = \delta_{rs}; \qquad r,s = \overline{1,g}. \tag{9}$$

The first-order corrections are given by

$$\begin{vmatrix} \langle\Psi_{k1}|H'|\Psi_{k1}\rangle - E_k^{(1)} & \langle\Psi_{k1}|H'|\Psi_{k2}\rangle & \cdots & \langle\Psi_{k1}|H'|\Psi_{kg}\rangle \\ \langle\Psi_{k2}|H'|\Psi_{k1}\rangle & \langle\Psi_{k2}|H'|\Psi_{k2}\rangle - E_k^{(1)} & \cdots & \langle\Psi_{k2}|H'|\Psi_{kg}\rangle \\ \vdots & \vdots & & \vdots \\ \langle\Psi_{kg}|H'|\Psi_{k1}\rangle & \langle\Psi_{kg}|H'|\Psi_{k2}\rangle & \cdots & \langle\Psi_{kg}|H'|\Psi_{kg}\rangle - E_k^{(1)} \end{vmatrix} = 0. \tag{10}$$

Roots: $E_{k1}^{(1)}, E_{k2}^{(1)}, \ldots, E_{kg}^{(1)}$.

If Ψ_{kr} are the eigenfunctions belonging to different eigenvalues of H', the matrix of H' will be diagonal.

The ground and excited states of helium

The Hamiltonian is split into two parts

$$H^0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2}, \tag{11}$$

$$H' = \frac{1}{r_{12}}. \tag{12}$$

0.1 Ground state

$$\Psi(r_1, r_2) = \psi_{1s}(r_1)\psi_{1s}(r_2). \tag{13}$$

$$H^0 = H_1^0 + H_2^0, \tag{14}$$

a

$$H^0\Psi = E_0\Psi \tag{15}$$

The Schrödinger-equation can be separated

$$H_i^0\psi_{1s}(r_i) = E_i\psi_{1s}(r_i); \quad i = 1, 2 \tag{16}$$

or

$$\left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right)\psi_{1s}(r_i) = E_i\psi_{1s}(r_i); \quad i = 1, 2. \tag{17}$$

hydrogenlike ion

$$\begin{aligned} E_i &= -\frac{Z^2}{2} && (18) \\ \psi_{1s}(r_i) &= \sqrt{\frac{Z^3}{\pi}}e^{-Zr_i}. && (19) \end{aligned}$$

0th order

$$E_0 = E_1 + E_2 = -Z^2 \tag{20}$$

lesz.

1st order

$$\begin{aligned} E^{(1)} &= \langle\Psi(r_1, r_2)|H'|\Psi(r_1, r_2)\rangle \\ &= \langle\psi_{1s}(r_1)\psi_{1s}(r_2)|\frac{1}{r_{12}}|\psi_{1s}(r_1)\psi_{1s}(r_2)\rangle. && (21) \end{aligned}$$

Result:

$$E^{(1)} = \frac{5}{8}Z \tag{22}$$

$$E = -Z^2 + \frac{5}{8}Z = -2,750 \text{ hartree} = -74,83 \text{ eV} \tag{23}$$

Experimental: $-2,90372$ hartree

0.2 Excited states of helium

$$\Psi_k(\mathbf{r_1},\mathbf{r_2}) = \psi_a(\mathbf{r_1})\psi_b(\mathbf{r_2}). \tag{24}$$

Parahelium ($S = 0$) the spin part is antisymmetric, the spatial wavefunction is symmetric

Orthohelium ($S = 1$) the spin part is symmetric, the spatial wavefunction is antisymetric

The unperturbed wavefunction

$$\Psi_k^+(\mathbf{r_1},\mathbf{r_2}) = \frac{1}{\sqrt{2}}[\psi_a(\mathbf{r_1})\psi_b(\mathbf{r_2}) + \psi_b(\mathbf{r_1})\psi_a(\mathbf{r_2})]; \quad S = 0 \tag{25}$$

$$\Psi_k^-(\mathbf{r_1},\mathbf{r_2}) = \frac{1}{\sqrt{2}}[\psi_a(\mathbf{r_1})\psi_b(\mathbf{r_2}) - \psi_b(\mathbf{r_1})\psi_a(\mathbf{r_2})]; \quad S = 1, \tag{26}$$

ψ_a and ψ_b hydrogenlike functions

$$E^0_{n_a n_b} = -\frac{Z^2}{2}\left(\frac{1}{n_a^2} + \frac{1}{n_b^2}\right). \tag{27}$$

$n_a = 1$, $n_b \equiv n$

$$E^0_n = -\frac{Z^2}{2}\left(1 + \frac{1}{n^2}\right). \tag{28}$$

$2n^2$ times degenerated unperturbed states

$H' = 1/r_{12}$

$$\det(\langle\Psi^\pm_{nlm}|H'|\Psi^\pm_{nl'm'}\rangle - \delta_{ll'}\delta_{mm'}\delta_{\pm\pm}E^{(1)}_n) = 0. \tag{29}$$

All nondiagonal elements will be zero

$$\begin{aligned}
\langle\Psi^+_{nlm}|\frac{1}{r_{12}}|\Psi^-_{nl'm'}\rangle &= \\
= \frac{1}{2}[\langle\psi_{100}\psi_{nlm}|\frac{1}{r_{12}}|\psi_{100}\psi_{nl'm'}\rangle &+ \langle\psi_{nlm}\psi_{100}|\frac{1}{r_{12}}|\psi_{100}\psi_{nl'm'}\rangle \\
-\langle\psi_{100}\psi_{nlm}|\frac{1}{r_{12}}|\psi_{nl'm'}\psi_{100}\rangle &- \langle\psi_{nlm}\psi_{100}|\frac{1}{r_{12}}|\psi_{nl'm'}\psi_{100}\rangle] \\
&= 0,
\end{aligned} \tag{30}$$

and

$$\begin{aligned}
\langle\Psi^\pm_{nlm}|\frac{1}{r_{12}}|\Psi^\pm_{nl'm'}\rangle &= \langle\psi_{100}\psi_{nlm}|\frac{1}{r_{12}}|\psi_{100}\psi_{nl'm'}\rangle \\
&\pm\langle\psi_{100}\psi_{nlm}|\frac{1}{r_{12}}|\psi_{nl'm'}\psi_{100}\rangle,
\end{aligned} \tag{31}$$

different from 0 only, if $l = l'$ and $m = m'$

The corrections are obtained by the diagonal elements

$$\begin{aligned} E^{(1)}_{nl\pm} &= \langle \Psi^{\pm}_{nlm} | H' | \Psi^{\pm}_{nl'm'} \rangle \\ &= \langle \psi_{100}\psi_{nlm} | \frac{1}{r_{12}} | \psi_{100}\psi_{nlm} \rangle \\ &\quad \pm \langle \psi_{nlm}\psi_{100} | \frac{1}{r_{12}} | \psi_{nlm}\psi_{100} \rangle \\ &= J_{nl} \pm K_{nl}. \end{aligned} \tag{32}$$

J_{nl} Coulomb term

K_{nl} exchange term

$$J_{nl} = \int_0^\infty dr_2 r_2^2 R_{nl}^2(r_2) \int_0^\infty dr_1 r_1^2 R_{10}^2(r_1) \frac{1}{r_>} \tag{33}$$

$$\begin{aligned} K_{nl} &= \frac{1}{2l+1} \int_0^\infty dr_2 r_2^2 R_{10}(r_2) R_{nl}(r_2) \\ &\quad \times \int_0^\infty dr_1 r_1^2 R_{10}(r_1) \frac{r_<^l}{r_>^{l+1}} R_{nl}(r_1), \end{aligned} \tag{34}$$

Finally

$$E_{nl\pm} = -\frac{Z^2}{2}\left(1 + \frac{1}{n^2}\right) + J_{nl} \pm K_{nl} \tag{35}$$

The enrgy of the ortho (triplet) state will be lower than the enrgy of the para (singlet) state

Ex: E_2^0 is split into 2^3S, 2^1S, 2^3P and 2^1P sublevels